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Panagiotis Voudouris  
*University of Athens*

Paul G. Spry  
*Iowa State University, [pgspry@iastate.edu](mailto:pgspry@iastate.edu)*

Vasilios Melfos  
*University of Thessaloniki*

Robert Moritz  
*Université de Genève*

Costas Papavassiliou  
*University of Athens*

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## Mineralogical Constraints on the Formation of the Perama Hill High-Sulfidation Epithermal Au-Ag-Te Deposit, Northeastern Greece

### Abstract

The Perama Hill deposit is a high- to intermediate-sulfidation Au-Ag-Te epithermal system hosted within silicic and argillic altered andesitic hyaloclastic rocks and overlying sandstones. New combined EPMA and fluid inclusion data from the deeper parts of the deposit suggest early deposition of native gold, Bi-chalcogenides (kawazulite/tetradymite solid solutions) and thioannates (probably at 291-349°C), followed by precious metal tellurides and electrum between 193 and 269°C. There is a trend from high- to intermediate-sulfidation state fluid conditions with time. The coexistence of both liquid- and vapor-rich inclusions homogenizing within the same temperature range demonstrates that boiling occurred during formation of the ore minerals. The kawazulite/tetradymite-gold association at Perama Hill suggests that it could have formed from a sulfide melt in the system Bi-Au-Se-Te system as gold was scavenged from the hydrothermal ore-forming fluid at elevated temperatures.

### Keywords

Epithermal, high-intermediate-sulfidation, bismuth tellurides-gold, gold-silver tellurides

### Disciplines

Geology | Mineral Physics | Volcanology

### Comments

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### Authors

Panagiotis Voudouris, Paul G. Spry, Vasilios Melfos, Robert Moritz, Costas Papavassiliou, and George Falalakis

# Mineralogical Constraints on the Formation of the Perama Hill High-Sulfidation Epithermal Au-Ag-Te Deposit, Northeastern Greece

**Panagiotis Voudouris**

*Department of Mineralogy-Petrology, University of Athens, Athens 15784, Greece, voudouris@geol.uoa.gr*

**Paul G. Spry**

*Department of Geological and Atmospheric Sciences, 253 Science I, Iowa State University, Ames, IA 50011-3212, USA*

**Vasilios Melfos**

*Department of Mineralogy, Petrology and Economic Geology, University of Thessaloniki, Thessaloniki, 54124, Greece*

**Robert Moritz**

*Section des Sciences de la Terre et de l'Environnement, Université de Genève, CH-1205 Genève, Switzerland*

**Costas Papavassiliou**

*Department of Economic Geology and Geochemistry, University of Athens, 15784 Athens, Greece*

**George Falalakis**

*Thracean Gold Mining S.A., 123 Demokratias Avenue, 68100 Alexandroupolis, Greece*

**Abstract.** The Perama Hill deposit is a high- to intermediate-sulfidation Au-Ag-Te epithermal system hosted within silicic and argillic altered andesitic hyaloclastic rocks and overlying sandstones. New combined EPMA and fluid inclusion data from the deeper parts of the deposit suggest early deposition of native gold, Bi-chalcogenides (kawazulite/tetradymite solid solutions) and thioestannates (probably at 291-349°C), followed by precious metal tellurides and electrum between 193 and 269°C. There is a trend from high- to intermediate-sulfidation state fluid conditions with time. The coexistence of both liquid- and vapor-rich inclusions homogenizing within the same temperature range demonstrates that boiling occurred during formation of the ore minerals. The kawazulite/tetradymite<sub>ss</sub>-gold association at Perama Hill suggests that it could have formed from a sulfide melt in the system Bi-Au-Se-Te system as gold was scavenged from the hydrothermal ore-forming fluid at elevated temperatures.

**Keywords.** Epithermal, high-intermediate-sulfidation, bismuth tellurides-gold, gold-silver tellurides

## 1 Introduction

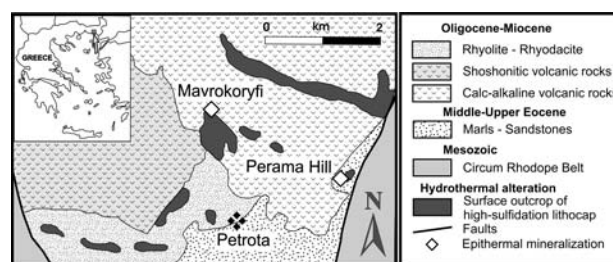
The Perama Hill epithermal gold deposit is located about 20km west of Alexandroupolis, northeastern Greece. Of major importance for the total resource of the deposit, and also for its genetic interpretation, is the presence of sulfide-rich mineralization found in drill holes in deeper levels of the deposit. Voudouris et al. (2007) studied the telluride and sulfosalt mineralogy of the Perama Hill deposit and discovered the presence of hessite, petzite, sylvanite and krennerite, and their genetic relationship to nearby epithermal-porphyry prospects in western Thrace.

The current study presents new paragenetic and compositional data on the tellurides, sulfides and sulfosalts from the Perama Hill deposit. Preliminary microthermometric data of quartz and barite from the sulfide mineralization give additional information on the

physico-chemical conditions of the hydrothermal fluids responsible for the deposition of tellurides and sulfosalts in the porphyry to epithermal environment.

## 2 Geological Setting

Ore deposits in northeastern Greece were formed during the final extensional stage of Tertiary orogenic collapse, which led to the formation of metamorphic core complexes, block faulting and widespread Oligocene-Miocene silicic to intermediate magmatism and magmatic-hydrothermal mineralization (Marchev et al. 2005).



**Figure 1.** Generalized geologic map of the Perama Hill area (Arikas and Voudouris 1998)

The Perama Hill deposit is located in the northeastern part of the Tertiary Petrota graben in contact with the NNE-trending eastern graben fault (Fig. 1). The Petrota graben is mainly covered by calc-alkaline and shoshonitic volcanic rocks (Arikas and Voudouris 1998). In the central and eastern part of the Petrota graben, a sequence of andesitic-dacitic volcanic breccias, including subaqueous andesite domes, flows and hyaloclastic rocks, rest on Late Priabonian turbiditic limestones, and is overlain and partly reworked by the Perama sandstones (Voudouris and Skarpelis 1998; Skarpelis et al. 1999; Lescuyer et al. 2003; Michael and Dimitroula 2004). The Perama sandstone is considered

to have been deposited in a palustrine environment (Lescuyer et al. 2003).

### 3 Mineralization and Alteration

Two different styles of mineralization are present in Perama Hill: (a) structurally controlled sulfide-bearing vein-type mineralization in the subaqueous andesites, and (b) stratabound, but structurally controlled, oxidized mineralization in the overlying sandstones (Voudouris and Skarpelis 1998; McAlister et al. 1999; Skarpelis et al. 1999; Lescuyer et al. 2003; Voudouris et al. 2007). Beneath the oxidized ore (below 100m), Lescuyer et al. (2003) distinguished two stages of hypogene alteration: Stage I consists of massive crystalline silicified rock and kaolinite-illite alteration with pyrite and marcasite, whereas Stage II is composed of banded veinlets of silica and barite that contain enargite-luzonite-stannite group minerals, covellite, Au-Ag tellurides, native gold, pyrite, galena and tetrahedrite.

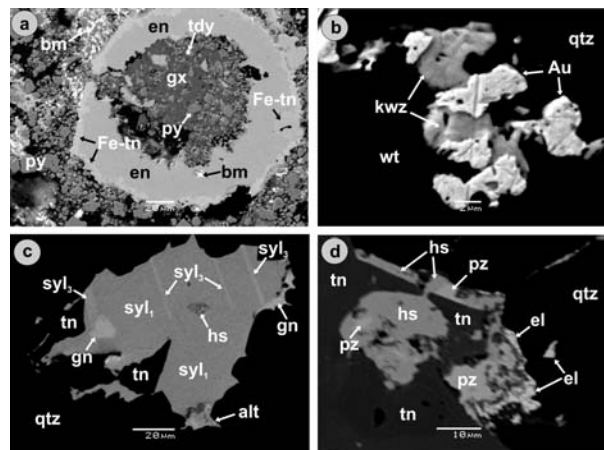
Paragenetic relationships during the present study suggest an early stage related to the deposition of marcasite, pyrite, enargite/luzonite, ferrian tennantite, watanabeite, Fe-poor sphalerite, covellite, kesterite, bismuthinite, lillianite homologues, selligmanite, jordanite, kawazulite, tetradymite and native gold, and a subsequent stage that contains zincian tennantite, galena, hessite, petzite, stützite, sylvanite, altaite, and electrum. The phosphates kolbeckite (Lescuyer et al. 2003) and gorceixite (this study), both members of the alunite supergroup minerals, are spatially related to enargite and pyrite.

### 4 Ore mineralogy

Pyrite (colloform, framboidal, euhedral), sphalerite (with <0.1 mole % FeS), galena, covellite and bismuthinite (with up to 15.9 wt. % Se), form part of the ore zone. Enargite/luzonite occur either intergrown with bismuthinite and Fe-rich tennantite (also in microchimneys (Fig. 2a) or as late phases post-dating galena, Zn-rich tennantite, sylvanite, and electrum. A watanabeite-like phase  $[\text{Cu}_4(\text{As,Sb})_2\text{S}_5]$ , kuramite ( $\text{Cu}_3\text{SnS}_4$ ), and kesterite  $[\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4]$ , are closely related to intergrowths of native gold (3.7 to 5.2 at. % Ag) and kawazulite-tetradymite solid solutions (Fig. 2b). Tetradymite (with up to 1.9 wt. % Se, Table 2) occurs as blebs (up to 5  $\mu\text{m}$ ) in the enargite-rich ore, included in quartz and gorceixite (Fig. 2a). Lillianite homologues form irregular grains spatially associated with bismuthinite, and included and replaced by zincian tennantite and galena.

Of the tellurides previously discovered by Voudouris et al. (2007), sylvanite ( $\text{AgAuTe}_4$ ) is the most abundant where it occurs in complex intergrowths with galena, zincian tennantite and other tellurides (Fig. 2c). The Au content of sylvanite ranges between 25.7 and 34.8 wt. % and Ag between 5.4 and 13.7 wt. %. Both Ag-rich and Ag-poor sylvanites (the latter compositionally overlapping with krennerite) were detected and classified as Syl-1 (close to stoichiometric; 0.7-1.0 a.p.f.u. Ag); Syl-2 (low-Ag; 0.4 to 0.7 a.p.f.u. Ag) and Syl-3 (very low Ag; 0.2 to 0.4 a.p.f.u. Ag) in accordance with the

terminology of Ciobanu et al. (2004). In some patches of sylvanite, lamellar alternations between Ag-rich (Syl-1) and very low Ag sylvanite (Syl-3) were observed (Fig. 2c). Hessite ( $\text{Ag}_2\text{Te}$ ) is intimately associated with petzite ( $\text{Ag}_3\text{AuTe}_2$ ), stützite ( $\text{Ag}_{5-x}\text{Te}_3$ ), stoichiometric sylvanite (Syl-1) and altaite ( $\text{PbTe}$ ). Electrum (20 to 27 at. % Ag), is accompanied by galena, and also occurs in contact with hessite and petzite (Fig. 2d).



**Figure 2.** Photomicrographs of ore associations at Perama Hill: (a) Micro-chimney composed, from rim to core, of Fe-rich tennantite (Fe-tn), enargite (en) and late pyrite (py), bismuthinite (bm), tetradymite (tdy) and gorceixite (gx) (SEM-BSE image, PD43); (b) Intergrowth of kawazulite (kwz), watanabeite (wt), kuramite (km) and native gold (Au) (SEM-BSE image, PD15); (c) Lamellar intergrowth of sylvanite-1 ( $\text{syl}_1$ ) and sylvanite-3 ( $\text{syl}_3$ ) associated with galena (gn), altaite (alt), hessite (hs), tennantite (tn) within quartz (qtz) (SEM-BSE image, PD1b); (d) Petzite (pz), hessite (hs) and electrum (el) associated with tennantite (tn) and quartz (qtz) (SEM-BSE image, PD11V).

### 5 Discussion

Two types of fluid inclusions were observed in vein quartz: liquid-rich aqueous inclusions and vapor-rich aqueous inclusions. Liquid-rich aqueous inclusions were also observed in barite.

Preliminary microthermometric analyses of fluid inclusions in quartz associated with sulfides show two ranges of homogenization temperature ( $T_h$ ): 193-269°C, with a peak at 250°C, and 291-349°C, with a peak at 320°C. Liquid-rich and vapor-rich inclusions homogenized within the same temperature range demonstrating that boiling occurred during ore mineral formation.  $T_h$  for inclusions in barite are ~240°C.

At Perama Hill, the deposition of native gold with Bi-sulfo-telluro-selenides preceded the deposition of gold-silver tellurides. The presence of tetradymite and kawazulite suggests that ore formation occurred under oxidizing conditions, similarly to other epithermal systems (e.g. Larga/Metaliferi Mountains, Romania), where native Te and Bi-Te melts ( $\text{Te} > \text{Bi}$ ) formed in deeper levels and/or higher temperature parts of the ore system (Ciobanu et al. 2004; Cook and Ciobanu 2004a, b). Bi-sulfosalts, Bi-chalcogenides (tetradymite and kawazulite), Sn-bearing minerals (kesterite, kuramite) and native gold at Perama Hill formed at  $T > 300^\circ\text{C}$ , in

accordance with the fluid inclusion data.

**Table 1. Representative electron microprobe analyses of tellurides and native elements**

	1	2	3	4	5	6	7
Au	0.52	21.21	25.72	30.33	33.82	98.99	83.48
Ag	61.25	45.53	12.06	8.43	5.66	2.10	13.02
Bi	0.05	0.25	0.14	0.14	0.22	nd	0.35
Cu	0.90	0.96	0.62	0.01	0.49	nd	0.71
Pb	0.10	0.02	0.14	0.11	bd	nd	0.88
Hg	bd	0.24	0.35	0.56	0.56	nd	1.45
Te	37.02	33.47	62.56	61.41	59.78	nd	0.05
Se	bd	bd	bd	bd	bd	nd	0.05
S	0.05	0.08	0.02	0.03	0.02	nd	0.29
Total	99.89	101.76	101.61	101.01	100.55	101.03	100.28
Atoms	3	6	6	6	6	1	1
Au	0.009	0.795	1.050	1.286	1.461	0.963	0.732
Ag	1.942	3.118	0.899	0.653	0.447	0.037	0.209
Bi	0.001	0.009	0.005	0.005	0.009	-	0.003
Cu	0.049	0.112	0.078	0.001	0.066	-	0.019
Pb	0.002	0.001	0.006	0.004	0.000	-	0.007
Hg	0.000	0.009	0.014	0.023	0.024	-	0.012
Te	0.992	1.938	3.943	4.020	3.987	-	0.001
Se	0.000	0.000	0.000	0.000	0.000	-	0.001
S	0.005	0.019	0.004	0.007	0.006	-	0.016

1 Hesseite; 2 petzite; 3 sylvanite-1; 4 sylvanite-2; 5 sylvanite-3; 6 native gold; 7 Electrum; nd not determined; bd below the limits of detection

During the second stage of ore deposition (193-269°C), gold-silver tellurides, zincian tennantite and galena were deposited. This is in accordance with observations made in several high-sulfidation deposits worldwide, where Au-Ag tellurides were introduced by fluids of intermediate-sulfidation state within the stability field of tennantite/tetrahedrite (Hedenquist et al. 2000). However, at Perama Hill, some Au-Ag tellurides were deposited under high-sulfidation conditions during a late luzonite/enargite-forming stage.

Ciobanu et al. (2004, 2005, 2007) and Cook et al. (2007) emphasized the role of melts in the systems Au-Bi-Te or Au-Pb-Te, which may play an important role in scavenging Au from hydrothermal fluids. At Perama Hill, the kawazulite/tetradymite<sub>ss</sub>-gold association suggests that the precursor phase could have been derived from a sulfide melt in the system Bi-Au-Se-Te system that could have scavenged gold from the hydrothermal fluids. Precipitates crystallized from fluids as a sulfide liquid (melt) at temperatures above the solvus curve/melting point of the precipitate, but below the melting point of individual components and/or their binary eutectics. Until now, the role of specific magma types, and especially of the rhyolitic magmatism, to the metal budget of the western Thrace mineralization has remained speculative. However, similar high- to intermediate-sulfidation epithermal Te- and Se-bearing epithermal mineralization at Prasolovskoye, Kuril Island (Kovalenker and Plotinskaya 2005), and the intrusion-related mineralization at Panormos Bay/Tinos Island, Greece (Tombros et al. 2007) similarly contain Sn-bearing minerals and Au-Ag-tellurides.

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